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Lithium Anode Limited Cycle
Secondary Battery

Quarterly Technical Progress Report No.2

15 December 1963

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FOREWORD

The work described in this report was accomplished in the Electrochemistry group, Materials Sciences Laboratory, Lockheed Missiles & Space Company, Palo Alto, California, for the Vehicle Power Branch, Air Force Aero Propulsion Laboratory, Research and Technology Division, United States Air Force, Wright-Patterson Air Force Base, Ohio, on Contract No. AF 33(657)-11709, Task 817304-20. Mr. W. S. Bishop of the AF Aero Propulsion Laboratory is project engineer for the project. This report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

1.0

INTRODUCTION

This experimental investigation on high-energy battery development has the objective of development of a cell capable of meeting a specific space flight application. Cells with lithium anodes and cupric fluoride or cobalt fluoride cathodes are to be investigated on this program. Significant goals are a battery discharging between 22 and 30 volts within a temperature range of 30 to 100°F and delivering 300 watt hour/pound. The steady discharge rate is 14.4 amperes with an additional 12 ampere load imposed for 10 minutes every 90 minutes. A recharge and additional discharge is required from the battery.

Presently available primary batteries will deliver about 100 watt hour/pound during discharges suitable for space applications. This is about 50 percent of the theoretical energy available from this system (AgO-Zn). The theoretical energy of the Li-CuF₂ couple is 746 watt hour/pound and of the LiCoF₃ couple 970 watt hour/pound. Achievement of the ultimate goals of this project would triple the useful flight time of space vehicle using a primary battery power system, or allow the equivalent increase in instrument load weight.

The electrolyte, anode and cathode for this system have been investigated and cells have been designed, built, and tested on the basis of experimental data.

2.0

SUMMARY

Solutions of sodium hexafluorophosphate (NaPF₆) in propylene carbonate or butyrolactone have conductivities ($6 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ and $13 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$) sufficiently high to make them useful in cells. Stainless steels and aluminum resist corrosion in these solutions and may be used as materials of construction. Polyolefin and polyester non-woven fabrics are stable and may be used as separators.

Lithium anodes in propylene carbonate - NaPF₆ show polarization increases of less than 200 millivolts during a 100 hour discharge at 10 ma/in² and utilization of over 85 percent of active material. Cupric fluoride electrodes may be discharged at 1 ma/in² and utilization of 30 percent obtained with approximately 1.5 volts polarization.

Electrode test results were used to design, construct and test cells with lithium anodes and cupric fluoride cathodes. A cell in this group completed 33 90-minute cycles (45 hours) to a 2.0 volt endpoint during the pulse discharge. This was equivalent to 13.5 percent utilization of CuF₂. This cell delivered, to the 2.0 volt endpoint, 10 watt hour/pound of actual electrode and electrolyte used in the test.

3.0 EXPERIMENTAL WORK AND DISCUSSION

3.1 Electrolyte Studies

3.1.1 Properties of Propylene Carbonate and Butyrolactone Solutions

Solubility and conductivity measurements were made of lithium tetrafluoroborate (LiBF_4) and lithium hexafluorophosphate LiPF_6 dissolved in butyrolactone, propylene carbonate, and nitromethane. A summary of conductivities of saturated solutions of these salts with NaPF_6 as a comparison is given in Table 1.

TABLE 1

Conductivities of Saturated Salt Solutions in Butyrolactone, Propylene Carbonate, and Nitromethane at 24°C

<u>Salt</u>	<u>Solvent</u>	<u>Concentration Moles/Liter</u>	<u>Specific Conductivity $\text{Ohm}^{-1} \text{ cm}^{-1}$</u>
LiBF_4	Butyrolactone	0.25	3.40×10^{-3}
LiPF_6	Butyrolactone	0.22	4.07×10^{-3}
NaPF_6	Butyrolactone	1.14	13.40×10^{-3}
LiBF_4	Propylene Carbonate	0.42	2.54×10^{-3}
LiPF_6	Propylene Carbonate	0.55	4.49×10^{-3}
NaPF_6	Propylene Carbonate	0.79	6.03×10^{-3}
LiBF_4	Nitromethane	0.11	0.23×10^{-3}
LiPF_6	Nitromethane	0.23	6.78×10^{-3}

Nitromethane has been eliminated as an electrolyte solvent because of instability. The lithium salts offer no advantages over NaPF_6 in propylene carbonate and butyrolactone and no further experimentation is intended with the lithium salts.

3.1.2

Properties of Propylene Carbonate - Sodium Hexafluorophosphate Solutions

The conductivity of NaPF_6 -propylene carbonate solutions with varying concentration of NaPF_6 was experimentally determined. A maximum conductivity is obtained at less than saturation for AlCl_3 - LiCl -propylene carbonate and it was possible that NaPF_6 solutions would behave similarly. Figure 1, which plots the results of these tests, shows maximum conductivity is obtained at maximum salt concentration. Evidently, the solubility of the NaPF_6 is so low that the viscosity of such solutions is not great enough to affect conductivity adversely.

The effect of temperature upon conductivity of NaPF_6 -propylene carbonate solutions is shown for two NaPF_6 concentrations in Figure 2. A linear temperature-conductivity relationship exists over the range 0 - 65°C; an increased slope is observed for the more concentrated solution.

The resistance of materials of construction to attack by a propylene carbonate - NaPF_6 solution was determined by storing samples of the material in the electrolyte at 165°F and measuring the weight change. There was darkening of the electrolyte in all cases after 12 days storage and the glass storage bottle was attacked. The darkening is probably associated with decomposition of propylene carbonate, but the products and effect on cell operation have not been determined. Table II summarizes the results of this test after 12 days and after 22 days of storage. Stainless steel and aluminum appear suitable for use in contact with propylene carbonate - NaPF_6 electrolyte while the use of nickel, copper, and silver are marginal.

3.1.3

Properties of Butyrolactone - Sodium Hexafluorophosphate Solutions

The effect of concentration of NaPF_6 in butyrolactone on the conductivity of these solutions is shown in Figure 3. As with propylene carbonate- NaPF_6 solutions, no maximum is observed, but the slope is quite low at maximum concentration. The conductivity of the saturated butyrolactone solution is almost twice that of the propylene carbonate solution.

The effect of temperature on conductivity of butyrolactone NaPF_6 solutions is shown in Figure 4. The relationship is linear between 0 and 55°C with a steeper slope for the more concentrated solutions.

TABLE II

Stability of Materials of Construction in NaPF_6 -Propylene Carbonate (0.75 moles/liter) Electrolyte at 165°F

Material	Form	Area Sq. In.	Weight Loss After 12 Days Storage		Weight Loss After 22 Days Storage	
			mg.	mg./in ² /day	mg.	mg./in ² /day
Copper	99+%	0.531	7.4	1.2	13.1	1.1
Nickel	99.9%	0.505	3.3	0.5	9.8	0.9
Silver	99+%	0.502	6.1	1.0	10.1	0.9
Aluminum	#1100	0.524	0	0	0.6	0.1
Soft Solder	60Sn 40Pb	0.570	23.0	3.4	41.5	3.3
Stainless Steel	#316	-----	+0.1	0	0.1	---
Stainless Steel	#304	-----	0.1	---	0	0
Hard Solder	Ag Cu Cd	0.389	3.2	0.7	8.0	0.9

TABLE III

Stability of Materials of Construction in NaPF₆-Butyrolactone (0.65 moles/liter) Electrolyte at 165°F

Material	Form	Area Sq. In.	Weight Loss After 12 Days Storage		Weight Loss After 22 Days Storage	
			mg.	mg./in ² /day	mg.	mg./in ² /day
Copper	99+%	0.531	61.3	9.6	66.6	5.7
Nickel	99.9%	0.505	11.8	1.9	23.0	2.1
Silver	99+%	0.502	5.0	0.8	12.0	1.1
Aluminum	#1100	0.524	0.4	0.1	2.2	0.2
Soft Solder	60Sn 40Pb	0.570	14.5	2.1	41.2	3.3
Stainless Steel	#316 Machined Ring	-----	0.1	---	0.5	---
Stainless Steel	#304 50 Mesh Screen	-----	0.1	---	0.4	---
Hard Solder	Ag Cu Cd	0.389	2.1	0.5	10.2	1.2

The stability of materials of construction in butyrolactone- NaPF_6 electrolyte at 165°F was determined in the same manner as for propylene carbonate solutions and is summarized in Table III. Except for the solution containing the soft solder sample which became a dark brown, all solutions were quite dark and the glass bottle was attacked.

Solution containing no metal was also bakened when stored in glass or polyethylene. Degradation of the solvent was quite severe and in some cases resulted in gelling, probably because of silicate dissolution. The effect of the solvent degradation on cell performance has not been determined but alternate electrolytes should be more thoroughly investigated. The corrosive effects of the butyrolactone solutions appear greater than the propylene carbonate solutions although stainless steels are quite inert and aluminum resists attack sufficiently to be useful.

3.2

Lithium Polarization Tests

Test cells were assembled with two lithium electrodes and the cells driven by a constant current power supply, making one electrode anodic and one cathodic. The result of tests with NaPF_6 -propylene carbonate electrolyte at 10 ma/in^2 are shown in Figure 5. The electrodes had sufficient lithium for approximately 120 hours of discharge at this rate. Approximately 90 percent utilization was achieved with polarization levels below 200 millivolts. The polarization on the graph is the increase in polarization from the initial closed circuit reading. The change between anode and reference at open circuit conditions and initial reading contains both the activation polarization of the electrode and the IR drop caused by solution resistance between anode and the reference electrode and these values were not determined.

Similar polarization tests were made but with nitromethane- $\text{AlCl}_3\text{-LiCl}$ electrolyte. The open cells were discharged in an inert atmosphere glove box and there was some loss of solvent which was replaced as needed to maintain electrolyte level. Figure 6 shows the change in potential with time. The end of the discharge where polarization increased rapidly was obtained from a recorder tape that measured cell voltage only. The lithium present on the electrodes as weighed was sufficient for 140 hours of discharge at the 10 ma/in^2 rate. The discrepancy with that actually obtained is probably the result of inaccuracies in weighing in the glove box.

Table IV

Polarization Tests of CuF_2 Cathodes in NaPF_6 -Propylene Carbonate Electrolyte

Cell No.	Per Cent CuF_2 in Cathode Mix	Conductive Addition	Preparation	Grid	Powder Weight-g	OCV Volts	Current Density ma/in^2	Time in Hours to Polarisation of		
								0.5 Volts	1.0 Volts	1.5 Volts
8	40	Graphite	Pasted	40x40 Cu screen	13.8					
9	70	Graphite	Pasted	40x40 Cu screen	17.4					
10	80	Graphite	Pasted	40x40 Cu screen	14.0					
11	80	Graphite	Pasted	40x40 Cu screen	13.6					
12	50	Graphite	Pasted	40x40 Cu screen	22.0	3.5	10/8	< 18	< 16	< 16
13	50	Graphite	Pasted	40x40 Cu screen	12.0	3.5	10/8	< 16	< 16	< 16
16	50	Graphite	Cold Press.	40x40 Cu screen	10 g	3.5	10/6.25	< 1	--	--
17	50	Graphite	Cold Press.	40x40 Cu screen	10 g	3.5	6.25	< 1	2.5	4.0
18	50	Graphite	Cold Press.	40x40 Cu screen	10 g	3.3	6.25	1.3	3.0	4.0
19	50	Graphite	Cold Press.	10 FS x Cu	10 g	3.55	2	1	1.0	26.0
20	100	----	Cold Press.	10 FS x Cu	15 g	3.5	2	(1)	----	----

(1) Dropped below 2.0 volts under load

TABLE IV - continued

Cell No.	Per Cent Cu_2S in Cathode Mix	Conductive Additive	Binder	Preparation	Grid	Powder Weight-g	OCV Volts	Time in Hours to Polarization of			
								Current Density ma/in^2	0.5 Volts	1.0 Volts	1.5 Volts
21	100	-----	-----	Cold Press	10 FS Cu	1.5	3.5	1	1	5	-----
22 (2)	50	Cu	-----	Cold Press	10 FS Cu	3.0	3.6	1	1	6	13
23	100 Sieved	-----	-----	Cold Press	10 FS Cu	1.5	3.55	1	1	2	7
28	50	Graphite	Col. Graphite in Min Spirits	Pasted	40x40 Cu screen	3.0	3.5	1	1	6	24
29	50	Graphite	"	Pasted	40x40 Cu screen	3.0	3.55	1	1	31	36
32 (5)	50	Silver Flake	-----	Cold Press	40x40 Ag screen	3.0	3.5	1	1	3	20
33 (5)	50	Silver Flake	-----	Cold Press	40x40 Ag screen	3.0	3.5	1	1	3	39
34 (5)	50	Silver Flake	Col. Graphite in Min Spirits	Pasted	40x40 Ag screen	3.0	3.0	1	1	10	30

(2) At 8 ma for 1 hour initially

(5) Cell on open circuit over weekend during discharge

TABLE IV - continued

Cell No.	Per Cent CuF in Cathode Mix	Conductive Additive	Binder	Preparation	Grid	Powder Weight-g	OCV Volts	Current Density ma/in ²	Time in Hours to Polarization of		
									0.5 Volts	1.0 Volts	1.5 Volts
35 (5)	50	Silver Flake	Col. Graphite in Min Spirits	Pasted	40x40 Ag screen	3.0	3.5	1	1	3	15
36 (5)	50	Graphite	"	Pasted	40x40 Ag screen	3.5	3.5	1	1	4	15
37 (5)	50	Graphite	"	Pasted	40x40 Ag screen	3.5	3.55	1	1	7	35
38 (5)	60	Graphite	"	Pasted	40x40 Ag screen	3.0	3.55	1	1	27+	50
39 (5)	60	Graphite	"	Pasted	40x40 Ag screen	3.0	3.55	1	1	12	52
40 (3)	60	Graphite	"	Pasted	40x40 Ag screen	2.5	3.3	1	1	3	10
41 (3)	60	Graphite	"	Pasted	40x40 Ag screen	2.5	3.45	1	1	3	5
42	60	Graphite	1.5% Poly ethylene	Pasted Hot Pres.	40x40 Cu screen	2.5g	-----		1	1	1
43	60	Graphite	1.5% Poly ethylene	Pasted Hot Pres.	40x40 Cu screen	2.5g	-----		1	1	1

(3) Aluminum expanded metal for anode grid

(5) Cell on open circuit over weekend during discharge

TABLE IV - continued

Cell No.	Per Cent CuP_2 in Cathode Mix	Conductive Additive	Binder	Preparation	Grid	Powder Weight-g	OCV Volts	Current Density ma/in^2	Time in Hours to Polarization of		
									0.5 Volts	1.0 Volts	1.5 Volts
44	60	Graphite	0.75% Poly ethylene	Pasted Hot Pres.	40x40 Cu screen	2.5g			1	8	30
45	60	Graphite	0.75% Poly ethylene	Pasted Hot Pres.	40x40 Cu screen	2.5g		1			
46 (5)	60	Graphite	0.40% Poly ethylene	Pasted Hot Pres.	40x40 Cu screen	2.5g		1	4		25
47 (5)	60	Graphite	0.40% Poly ethylene	Pasted Hot Pres.	40x40 Cu screen	2.5g		1			
48 (4,5)	60	Graphite	0.40% Poly ethylene	Pasted Hot Pres.	40x40 Cu screen	2.5g		1			
49(4,5)	60	Graphite	0.40% Poly ethylene	Pasted Hot Pres.	40x40 Cu screen	2.5g		1	16		45

(4) Electrolyte was butyrolactone + NaPF_6

(5) Cell on open circuit over weekend during discharge

Table V

Polarization Tests of CoF_3 Cathodes in NaPF_6 -Propylene Carbonate Electrolyte

Cell No.	Per Cent CoF_3 in Cathode Mix	Conductive Addition	Preparation	Grid	Powder Weight	OCV Volts	Time in Hours to Polarization of			
							Current Density ma/in^2	0.5 Volts	1.0 Volts	1.5 Volts
14	50	Graphite	Paste	40x40 Ni screen	12 g	3.35	10/8	< 1	< 16	< 16
15	50	Graphite	Paste	"	12 g	3.35	10/8	< 1	< 16	< 16
30	50	Graphite	Paste	"	12 g	3.4	1	< 1	< 1	6
31	50	Graphite	Paste	"	12 g	1.3	1	---	---	---

Periodically during the discharge of these cells, the load was increased in steps to obtain polarization at higher discharge levels and then decreased in similar steps. Polarization curves obtained after 4, 49, and 100 hours of discharge are shown on Figure 7. The decrease in polarization between 49 and 100 hours of discharge occurred with both cells and is shown by the points on Figure 6. These data indicate that polarization of less than 200 millivolts is obtained with short-time higher current rates during a significant part of the discharge.

The driven cell tests require a reversible cathode to prevent electrolyte degradation. With the NaPF₆-propylene carbonate electrolyte, cathode polarization started at 1.0 volt and increased to over 5.0 volts at the end of the test. A similar cathode polarization was over 10.0 volts after 24 hours and the test was discontinued.

The deposition of lithium or sodium from the solution as the cathodic reaction evidently is not readily accomplished and potentials are reached which result in solvent decomposition.

From the results obtained with nitromethane and propylene carbonate electrolytes, it appears that the polarization for the anodic reaction



at current densities of 10 ma/in² or less will not seriously affect cell operation. Utilization of 85-95 percent of active material may be expected at these current densities. Tests with butyrolactone electrolyte at current densities of 1 ma/in² agree with these conclusions. The lithium electrode appears sufficiently developed at this point that additional effort may be more fruitfully applied to cathode development.

3.3

Cathodic Polarization Tests

3.3.1

Polarization of Cupric Fluoride Electrodes

Copper fluoride is a poor electronic conductor; consequently, the utilization characteristics of a thick massive copper fluoride cathode in a cell would be quite poor. Generally, cathodic materials used in electrochemical cells are finely powdered to increase the surface area and mixed with an electronic conductor to increase the points at which electrons can be supplied for the cathodic reaction. Another consideration

in making the electrode is the mechanical strength that will maintain the shape of the electrode and the contact between reaction sites and current carrying grid.

Cathodes for this contract have been fabricated by cold pressing of dry powder, by pasting the cathode mixture with added colloidal graphite suspended in mineral spirits as a binder, and by pasting a cathode mixture containing finely powdered thermoplastic resin, drying, and pressing above the flow point of the resin. All mixes other than 100 percent CuF_2 were ball milled for 16 hours. In some cases, CuF_2 as received was sieved through 100 mesh screen. Pasted electrodes were vacuum dried at 850-1000°C for four hours. Pressed electrodes were placed in a steel die in an inert atmosphere, the assembly sealed in aluminum foil and removed from the inert atmosphere. Pressure was applied in a hydraulic press. Uniform distribution of dry material was difficult, and this resulted in non-uniform pressure distribution in the pressing operation, particularly with thin electrodes, although some spots that maintained good adhesion and cohesion during discharge were found on these electrodes.

Cathodes were assembled with an anode of sheet lithium rolled on a silver expanded metal grid and a lithium reference electrode centrally situated between the electrodes. Glass fiber paper was used to separate the electrodes in the solution. Propylene carbonate - NaPF_6 electrolyte was used for all tests unless indicated otherwise.

A summary of polarization tests of CuF_2 cathodes is shown in Table II. The first four runs were made with heavy electrodes which cracked badly during handling and assembly. Microscopic examination of the 100 percent CuF_2 electrodes showed crystals of copper which indicated complete reduction of CuF_2 to copper during discharge.

Pasted electrodes performed somewhat better than the cold pressed electrodes. Disassembly of these test cells showed the cathode mix to be swollen and loosened from the grid. Electrodes with best adhesion (#29 vs #28) developed best polarization for equivalent time. Resin bonded electrodes were made to improve adhesion. These electrodes did not swell as did the pasted electrodes but adhesion to the grid was poor and cathode mix could be flaked from the

grid. The 1.5 percent polyethylene bonded cathodes had too high a resistance to sustain discharge but the results obtained from the 0.4 percent and the 0.75 percent resin content cathodes were favorable. Cathodes with 0.4 percent polyethylene binder were selected for cell tests with profile discharge.

3.3.2

Polarization of Cobaltic Fluoride Electrodes

A summary of CoF_3 electrodes tested is shown on Table V. These electrodes were pasted with graphite in mineral spirits as binder by the same technique as the CuF_2 electrodes and suffered similarly from poor adhesion and cohesion. These electrodes did not recover their open circuit voltage to the same extent the CuF_2 electrodes did when current was interrupted for extended times during discharge.

3.4

Separator Stability in Electrolyte

Various separator materials that had been found useful in nonaqueous electrolyte at room temperature were tested for stability at 165°F. These materials were selected from those that could be dried free of water and could be obtained in this and porous forms. Table VI which summarizes the tests indicates that polyester (DACRON) and polyolefin non-woven fabrics withstand exposure to the electrolyte and should be useful as separators in cells with propylene carbonate as butyrolactone based electrolytes.

3.5

Cell Tests

Based on previous work, two cells were designed and built for a profile discharge test. The current profile of the discharge was 80 minutes at 14.9 amperes followed by ten minutes at 26.9 amperes with the cycle continuously repeated. Lower currents were used for the discharge but in the same relative proportion. The cells were assembled in split polypropylene cases and had the following construction.

Anodes: 4, Lithium rolled on expanded silver sheet with final thickness of .020

Cathodes: 3, 60% CuF_2 , 39.6% graphite, 0.4% powdered 325 mesh polyethylene. Powder ball milled 16 hours and then pasted with 1% acrylic in xylol on expanded copper sheet. Pressed at 5T/in² at 300°F. 6.6 g cathode powder/electrode. Discharge current density 0.7 ma/sq in steady.

Separator: 1 thickness non woven polyester (DACRON) fabric

Electrolyte: .65 m/e NaPF_6 in Butyrolactone 32 cc in #51; 15 cc in #50 which had plastic spacer blacks added to fill the cavity.

Typical discharge cycles for Cell #51 are shown on Figure 8. Cell 51 had 33 cycles (45 hours) to a voltage endpoint of 2.0 volts during the high current pulse and Cell #50, 23 cycles (34.5 hours). Approximately 13.5% utilization of CuF_2 was achieved and based on the actual weight of electrodes and electrolyte, the energy to weight relationship was 10 wh/lb.

The major factor for the low energy to weight ratio was the poor utilization of the active cathode material. A smaller factor at this stage but of importance is the drop from open circuit voltage to discharge level indicating resistance in the electrolyte and in the cathode structure. The cathode structure and the electrolyte deserve further study.

Cell and Battery Design

Cell design calculations based on 17 ma/sq inch maximum current density were reported in the first quarterly report of this contract. The polarization measurements of lithium anodes are based on a steady discharge rate and are at a slightly higher rate; maximum discharge in this case during the high rate pulse would be 18.3 ma/sq in. A nine-cell battery to operate between 22 and 30 volts would allow a voltage range of 2.5 to 3.3 volts per cell. This allows 800 millivolts for polarization and IR losses in the cell during its discharge life. Data indicates that not over 200 millivolts loss will be incurred by polarization of the lithium anode, allowing 600 millivolts for cathode polarization and IR losses. Previously obtained data indicated that the minimum resistance with a separator saturated with electrolyte for nonaqueous cells is about 5.0 sq. in. At the pulse discharge rate of 18.3 ma/sq in., this would be a loss of 92 millivolts. There are therefore about 500 millivolts that may be lost by polarization and ohmic losses at the cathode within the allowable cell voltage range.

Current densities at which the cathodes are tested has been dropped from 10 ma/in² which was a design goal to 1 ma/in² in an effort to get test data for a 100 hour discharge. Decreasing the current density decreases the active material needed per unit area for a 100 hour discharge and consequently, the relative thickness. This decreases ohmic losses in the

electrode and may allow a higher active material ratio in cathodes where the active material is a non-conductor and must have an electronic conductor added. Lower current density also decreases ohmic losses in the electrolyte. The penalty for the lower current density is increased weight; additional inactive grid material is used, a greater weight of electrolyte and probably a larger cell case. Calculations based on 1 ma/in² current density show that 75-100 wh/lb of active material, grid and electrolyte may be achieved. Added active materials above theoretical capacity to the extent of 10 percent for the anode and 100 percent for the cathode are included in the calculation, but case and terminals are not. Current densities of 10 ma/in² must be achieved with usable voltage to obtain 300 wh/lb.

4.0 TRAVEL AND CONFERENCES

No conferences were held during the period covered by this quarterly report.

5.0 WORK PROGRAM FOR THIRD QUARTER

The general areas that will receive effort during the third quarter are fabrication of cathodes to sustain higher current densities and better utilization and further study to obtain more stable electrolyte compositions.

Improved cathode fabrication will be attempted by further study of resin binder in the cathode formulation and by incorporation of CuF₂ in a porous metal matrix.

Electrolyte decomposition and compatibility studies will be made at room temperatures and at a temperature intermediate to 165°F.

Second generation cells will be designed and constructed utilizing the results obtained from the experimental programs.

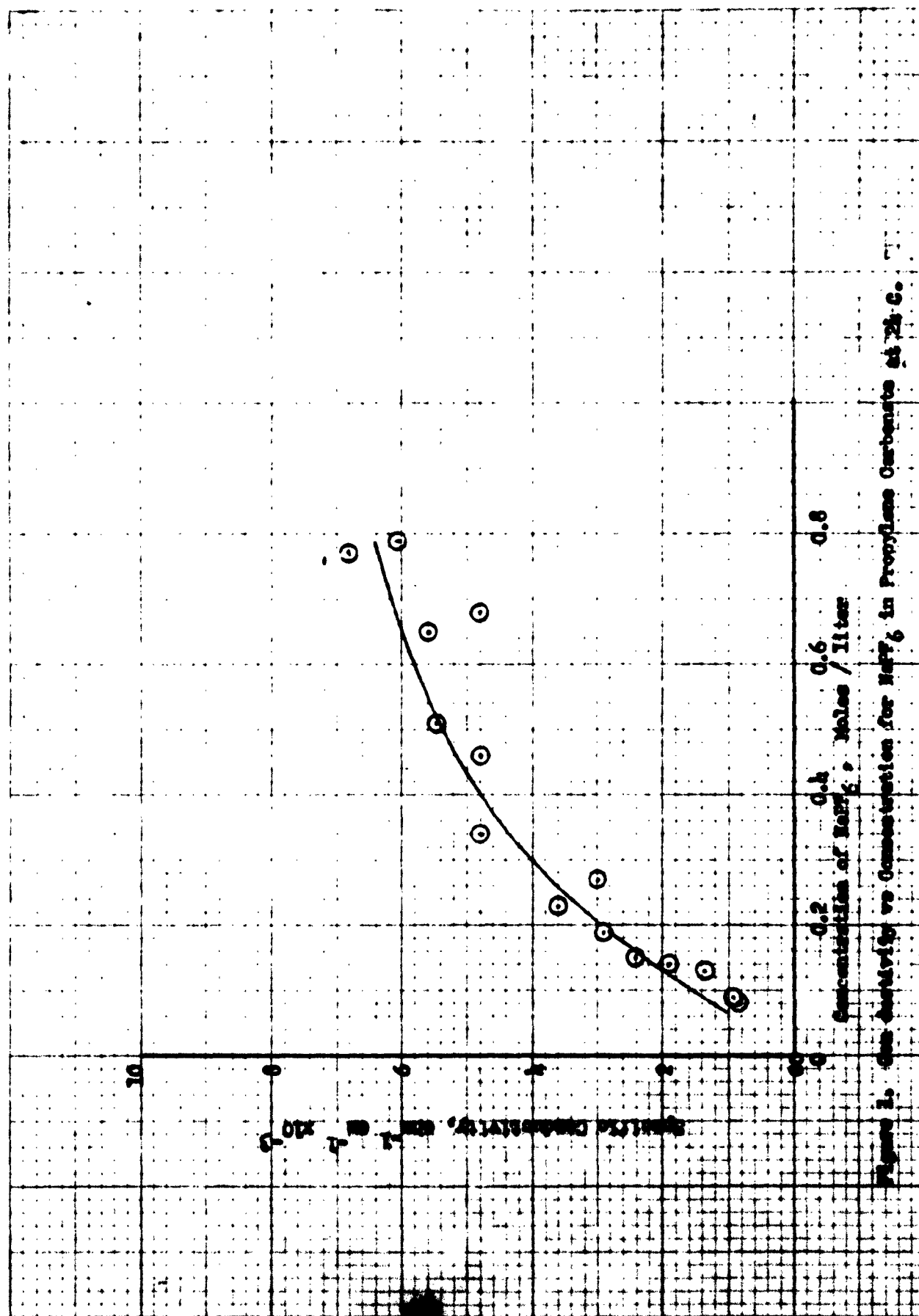


Figure 1. Gas Density vs Concentration for NaF_6 in Propylene Carbonates at 25°C.

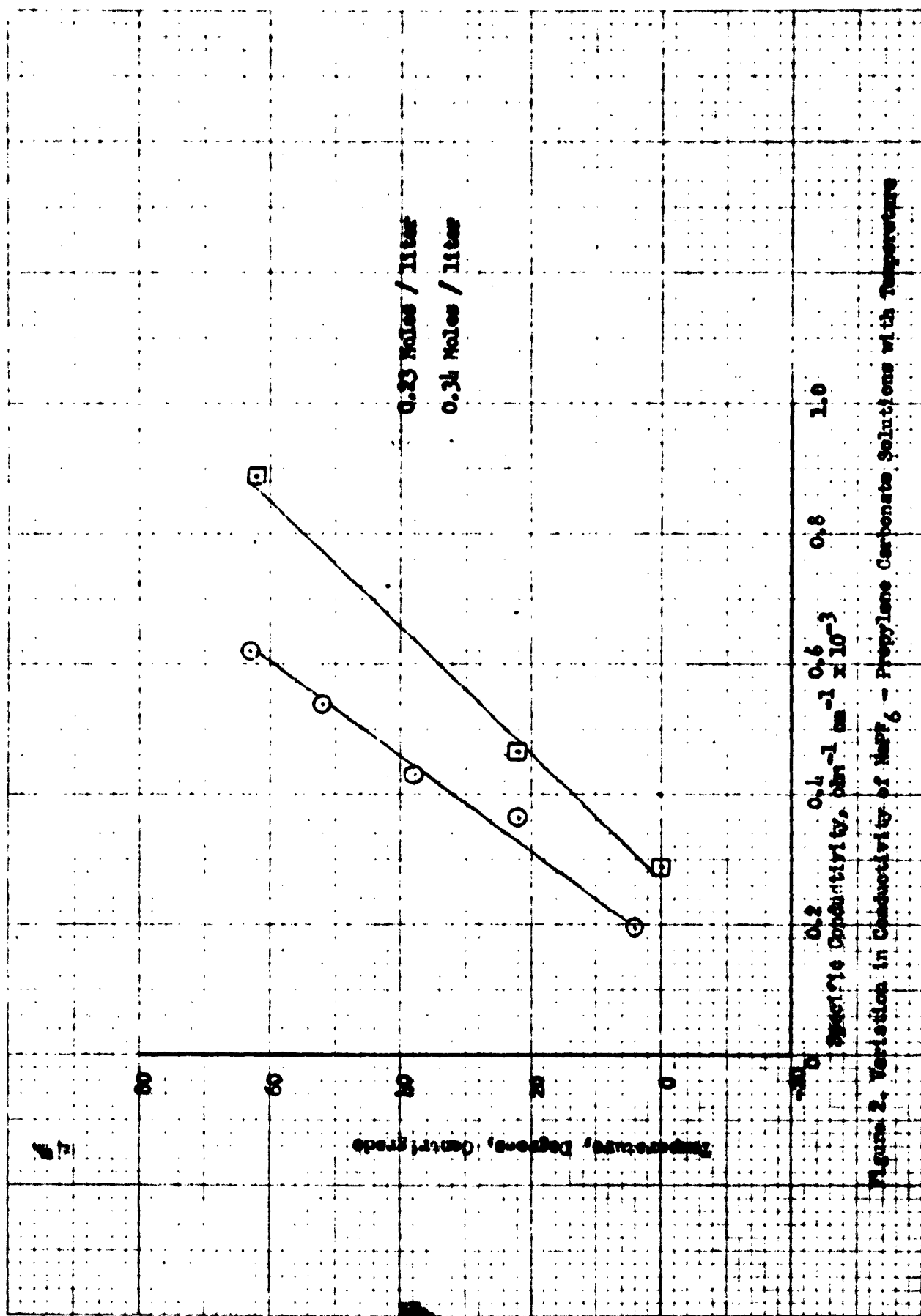


Figure 2. Variation in Conductivity of NaPF_6 - Propylene Carbonate Solutions with Temperature

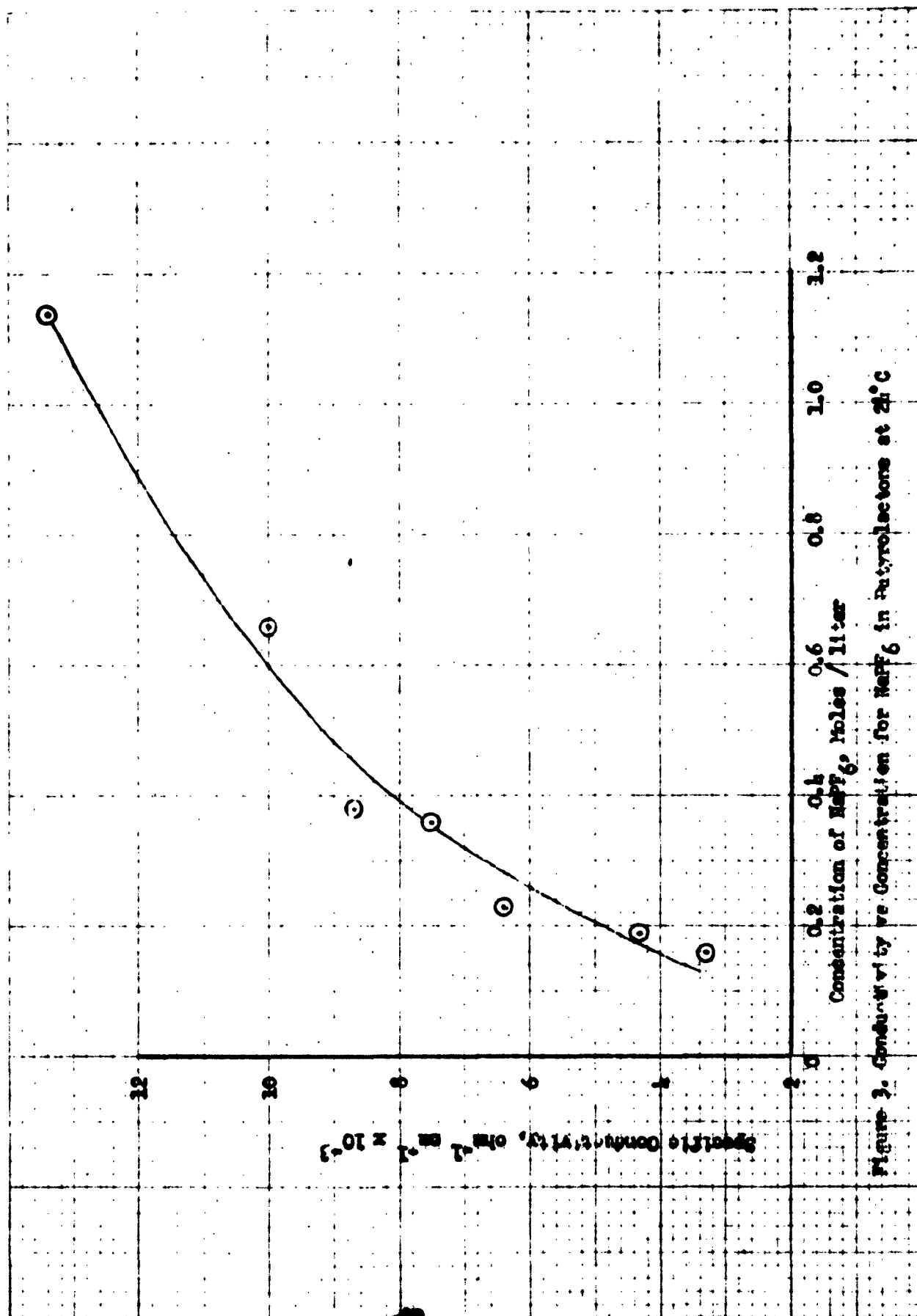
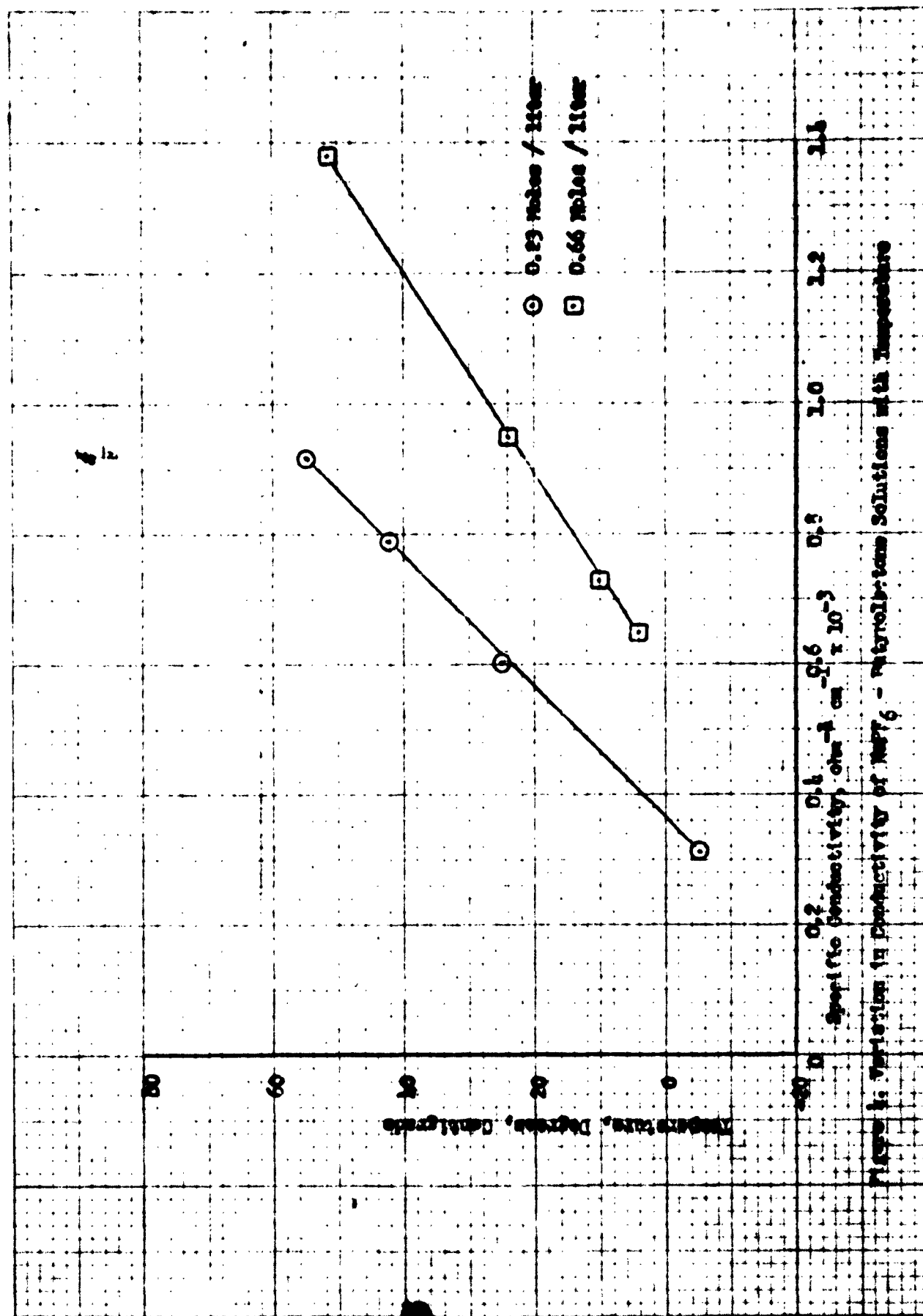
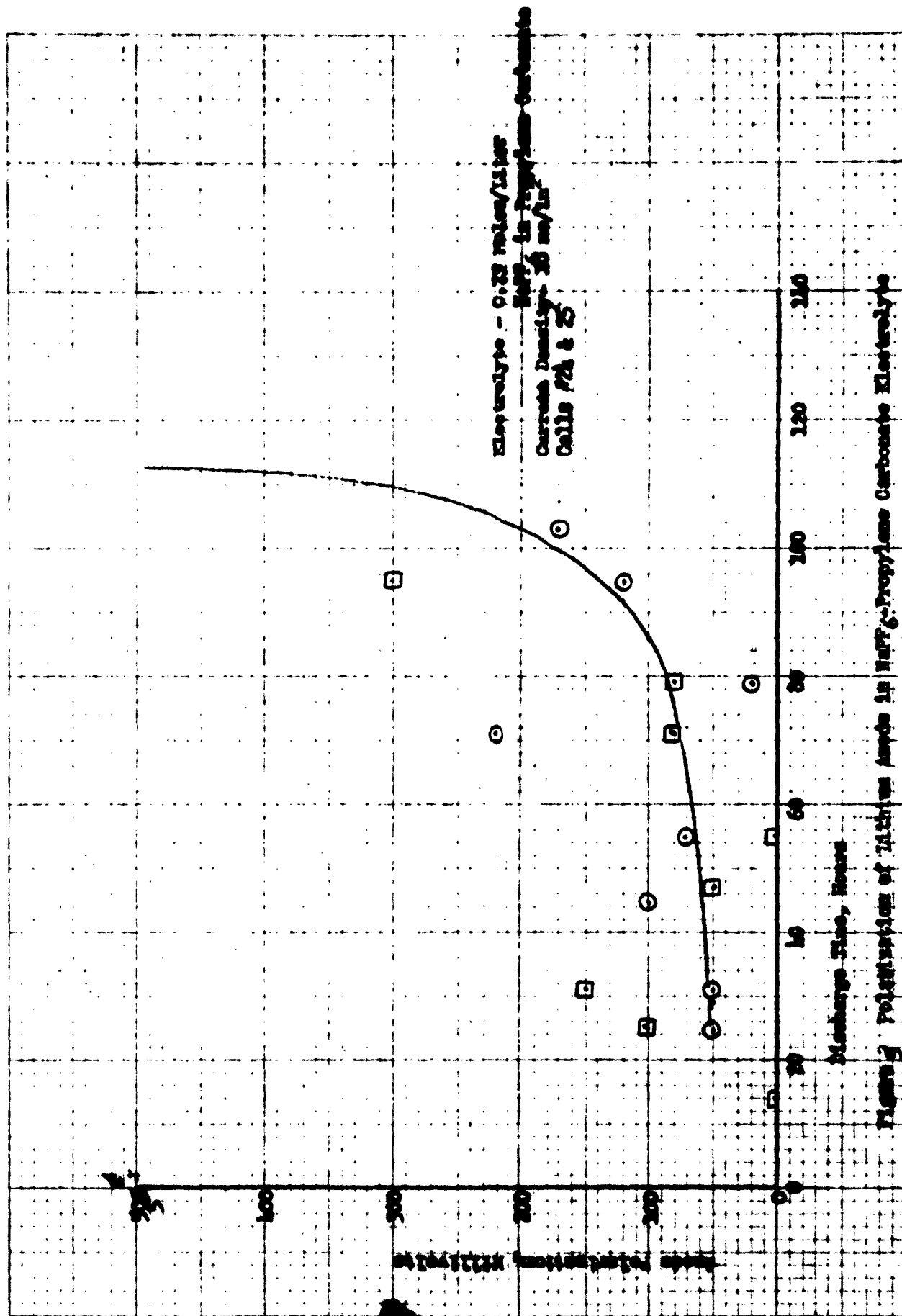


Figure 3. Conductivity vs. Concentration for NaPF_6 in Butyrolactone at 25°C

Figure 1: Variation in Conductivity of $\text{Na}_2\text{S}_2\text{O}_3$ - Potassium Sulfate Solutions with Temperature

NO 340-1C DIETZEN GRAPH PAPER
10 X 10 PER INCH

CUOTNE D ETZEN CO.



Discharge Time, Hours

Figure 2. Polarization of Nickel Anode in NiPP₆-Propylene Carbonate Electrolyte

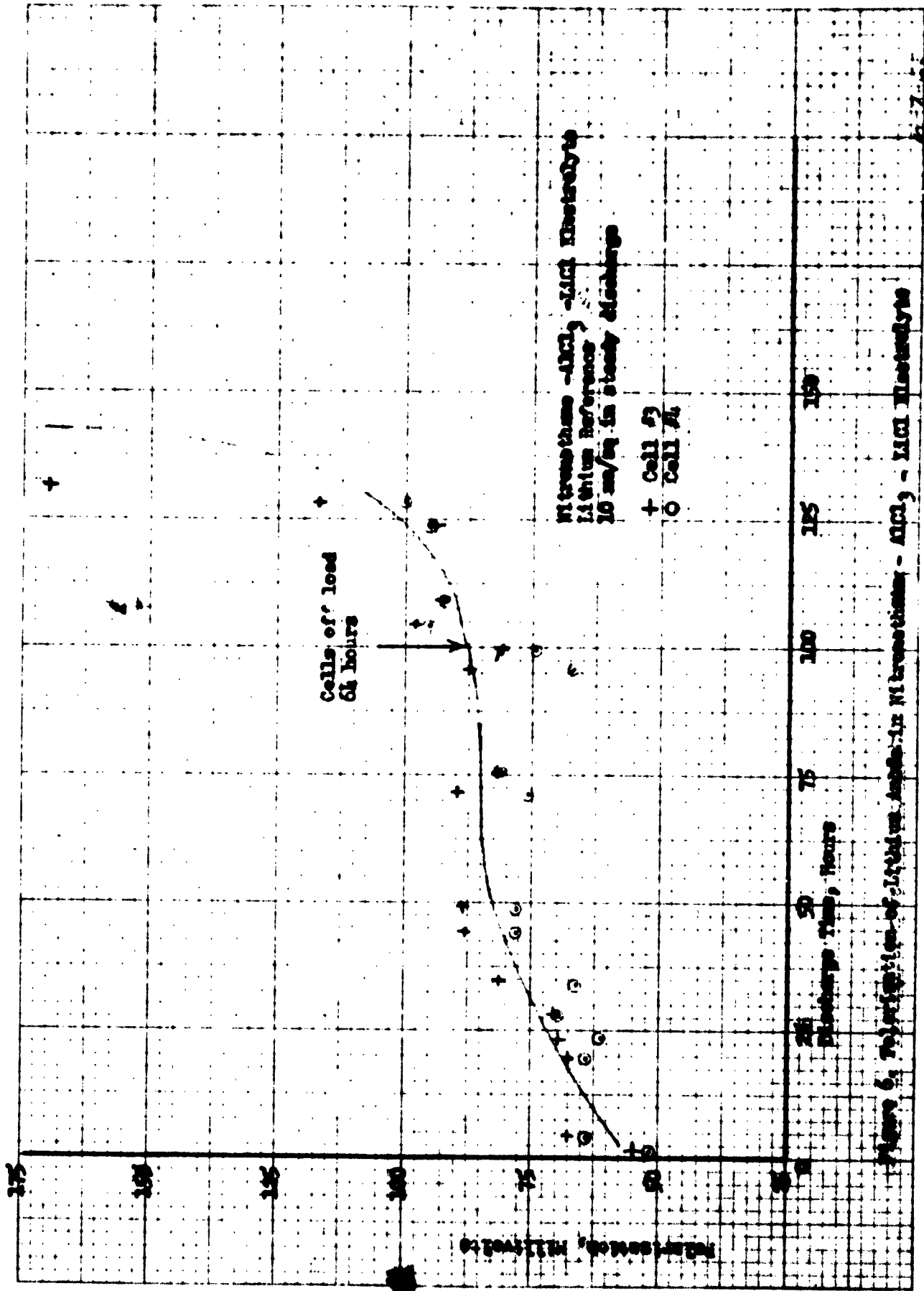
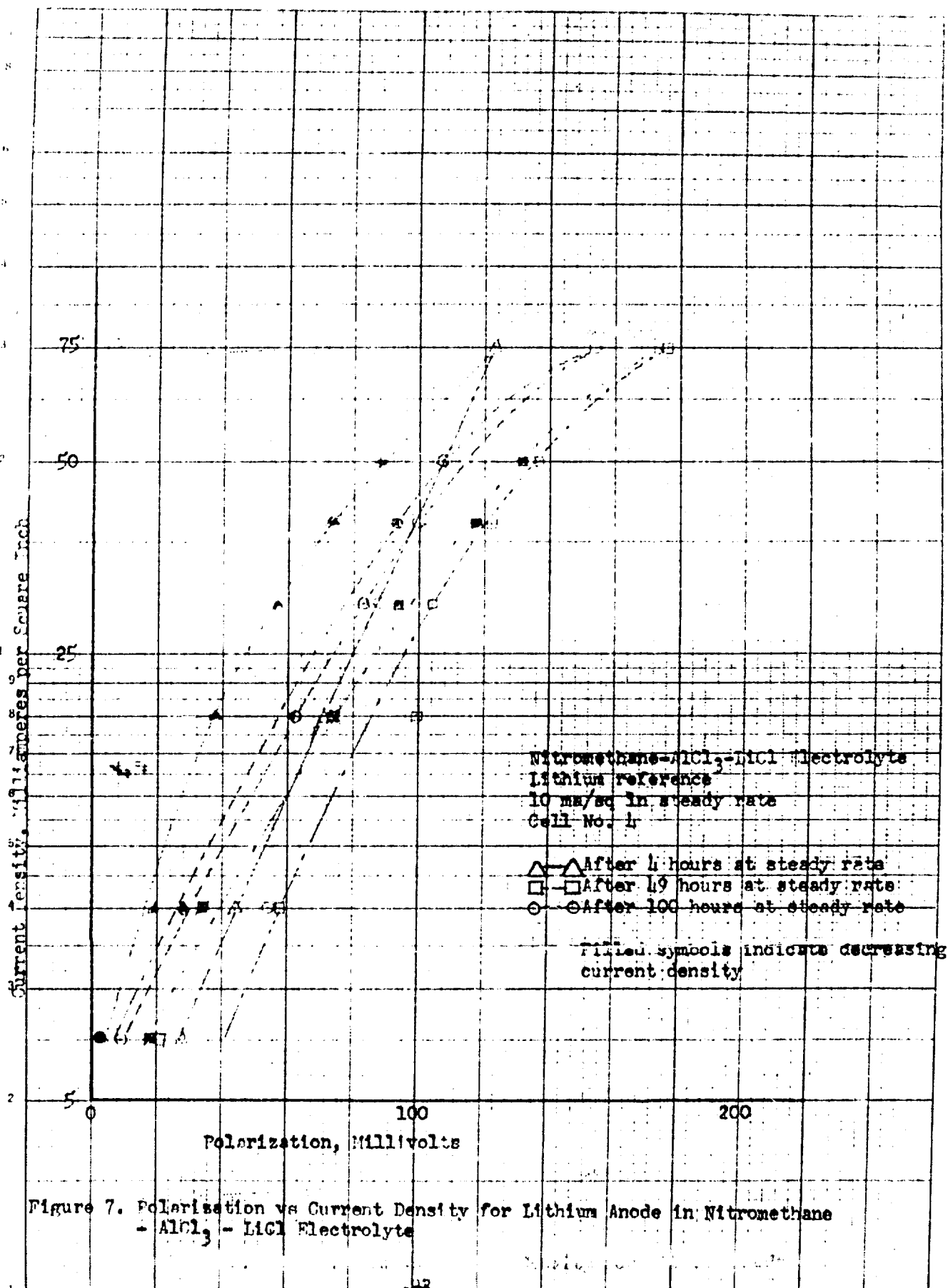


Figure 6: Relationship of Lithium Absorption in Nitroethane-AlCl₃ - LiCl Electrolyte



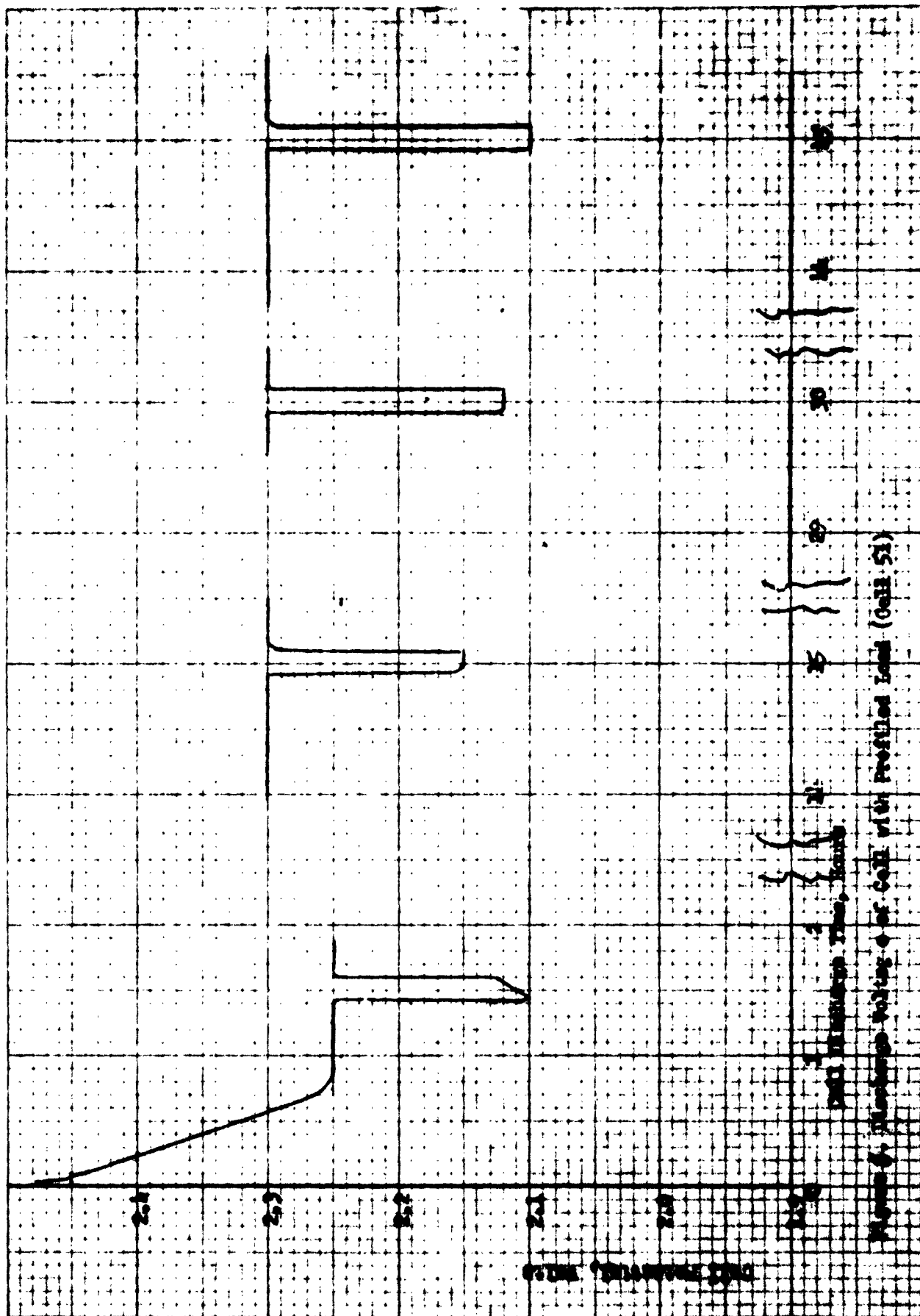


Figure 1. Waveform Voltage of Cell with Profiled Load (Cell 51)

Table VI
STABILITY OF SEPARATOR MATERIAL IN ELECTROLYTE SOLUTIONS AT 165°F

SAMPLE NO.	MATERIAL *	FORM	PROPYLENE CARBONATE SAT. WITH NaPF ₆		BUTYRO LACTONE SAT. WITH NaPF ₆	
			24 hours	14 day	48 hours	14 day
1	Glass	Fiber Matt	Disintegrated & sol.; soln yel	---	Disintegrated & sol.; soln br	--
2	Polyester	Fiber Matt	Material ok soln br.	material ok soln br	Material ok soln br	--
3	Polyester	"	"	"	Material ok soln lt. br	
4	Polyester	"	"	"	Material ok soln. yel	Material curled soln dk. br
5	Polyester	Film	Material ok soln br	Material ok soln br	Material ok soln br	
6	Polyamide	Fiber woven	Material sol; soln yel	---	Material ok soln yel	Material sol. soln yel
7	"	Fiber Matt	"	---	Material sol soln br	--
8	"	"	"	---	Material sol soln br	--
9	Acrylic	Fiber Matt	Material sol soln yel	---	Material sol soln br	--
10	Asbestos	Fiber Matt	Material ok soln yel	Mat. disint. or sol	Mat. disint. or sol	--
11	Polyolefin	Porous sheet	Material ok soln yel	Mat. ok soln yel	Mat. ok soln br	Mat. ok soln br
12	"	Woven screen	"	"	"	"
13	"	Porous sheet	"	"	"	"
14	"	Fiber Matt	"	"	"	"

Table VI (con't)
 STABILITY OF SEPARATOR MATERIAL IN ELECTROLYTE SOLUTIONS AT 165°F

SAMPLE NO.	MATERIAL *	FORM	PROPYLENE CARBONATE SAT. WITH NaPF ₆		BUTYRO LACTONE SAT. WITH NaPF ₆	
			24 hours	14 day	48 hours	14 day
15	Fluorinated Polyolefin	Woven screen	Material ok soln yel	Material ok soln yel	Material ok soln yel	Material ok soln yel
16	Acrylic	Fiber Matt			Mat. sol	--
17	Acrylic	Fiber Matt			mat. sol	--

*Trade designations listed on Appendix I

APPENDIX I

TRADE DESIGNATIONS OF SEPARATOR MATERIALS TESTED

<u>SAMPLE</u>	<u>CODE</u>	<u>SOURCE</u>
1	934-AH Filter Paper	Hurlbut Paper
2	Dacron EM343	Kendall Mills
3	Dacron EM345	Kendall Mills
4	Dacron EM346	Kendall Mills
5	Mylar	E. I. duPont
6	Nylon Cloth A3228/2	Stern & Stern Fabrics
7	Nylon 535-1-2	Huguet Fabrics
8	Nylon NY-SUL-SOFT1383ev	Star Woolen Co.
9	Orlon EM333	Kendall Mills
10	Quinterra Type 1	Johns-Manville Co.
11	Polyethylene 14PN	ESB-Reeves Corp.
12	Polyethylene P2200	National Filter Media
13	Polyethylene HI-250	Bel-Art Products
14	Polypropylene	American Felt Co.
15	Teflon T-2310	National Filter Media
16	Dynel EM307	Kendall Mills Co.
17	Dynel M-14M	Kendall Mills Co.

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